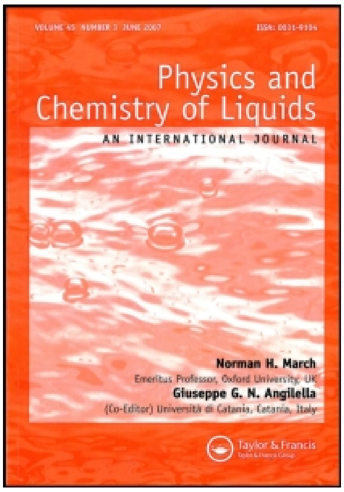

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article March, N. H.(1988) 'Ion Pair Neutralization: Solution of Smoluchowski Equation for Coulomb Field', Physics and Chemistry of Liquids, 18: 3, 227 — 233

To link to this Article: DOI: 10.1080/00319108808078596

URL: http://dx.doi.org/10.1080/00319108808078596

Phys. Chem. Liq., 1988, Vol. 18, pp. 227-233
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Printed in the United Kingdom

Ion Pair Neutralization: Solution of Smoluchowski Equation for Coulomb Field

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(Received 22 March 1988)

In pioneering work, Onsager solved the Smoluchowski equation to obtain the probability that a pair of ions in a dielectric medium will escape mutual neutralization in the long-time limit. In the present paper, an approximate solution of the Smoluchowski equation for a Coulomb field is constructed; general enough to allow the kinetics of the process to be treated. The connection with Onsager's treatment, and the later study of Mozumder, is briefly discussed.

Key Words: Coulomb field, dielectric constant.

1 INTRODUCTION

In pioneering work, Onsager[1] solved the Smoluchowski equation for a pair of ions in a dielectric medium. There he studied, in particular, the probability that the pair will escape mutual neutralization, in the long-time limit t tends to infinity. His result was that this probability as $t \to \infty$ is given by the reciprocal of the Boltzmann factor with respect to the pair potential energy calculated at the initial pair separation.

While Onsager gave the description of the steady-state situation in the extreme long-time limit, he did not concern himself with the kinetics of the process. To understand, for instance, radiation-induced luminescence in organic liquids, one needs to know such kinetics, as Mozumder[2] especially has emphasized. We shall adopt precisely the same framework as Mozumder as starting point; this is summarized in Section 2 below. Whereas Mozumder used the so-called method of "prescribed diffusion," we here propose an approximate solution transcending this, which is set out in Section 3. Section 4 constitutes a brief summary, together with suggestions for further work in this area.

2 SMOLUCHOWSKI EQUATION FOR A BARE COULOMB FIELD

To study the kinetics of charge neutralization within the framework of random walk in a Coulomb field, we follow Refs 1 and 2 by defining the probability $P(\mathbf{r}_0; \mathbf{r}, t)d\mathbf{r}$ that the ion pair will be between the distances $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$ at time t if the random walk started from a thermalization distance $\mathbf{r}_0$ at zero time. For time t considerably greater than the relaxation time for the random walk process, the above probability P satisfies the Smoluchowski equation[3] given by

$$\frac{\partial P}{\partial t} = D\nabla^2 P - f^{-1}\nabla \cdot (P\mathscr{F}). \tag{2.1}$$

Here the friction coefficient f is defined as the ratio of the impressed force to the drift velocity. Einstein[4] gave the relation between f and the diffusion constant D as

$$D = \frac{k_B T}{f}. \tag{2.2}$$

The mutual force $\mathscr{F}$ is taken in the present context to be given by Coulomb's Law:

$$\mathscr{F} = \frac{-e^2\mathbf{r}}{\varepsilon r^3}, \tag{2.3}$$

e being the magnitude of the electronic charge and ε the dielectric constant of the medium. Then one obtains from Eq. (2.1) the differential equation

$$\frac{\partial P}{\partial t} = D[\nabla^2 P + \alpha(\mathbf{r}/r^3) \cdot \nabla P], \tag{2.4}$$

where the length α, which is the distance at which the potential energy of the ions is numerically equal to $k_B T$, is given by

$$\alpha = e^2/\varepsilon k_B T; \tag{2.5}$$

the so-called Onsager length[2].

3 INTEGRAL EQUATION FORM OF SMOLUCHOWSKI EQUATION

In the limit $\alpha \to 0$, one has the solution, P_0 say, of Eq. (2.4) as

$$P_0(\mathbf{r}_0; \mathbf{r}, t) = \frac{\exp[-(\mathbf{r} - \mathbf{r}_0)^2/4Dt]}{(4\pi Dt)^{3/2}}. \tag{3.1}$$

The first important step in obtaining an approximate solution of Eq. (2.4) when $\alpha \neq 0$ is to convert it to integral equation form. This we can conveniently do by writing the probability P in the form

$$P = P_0 \exp(-tU). \tag{3.2}$$

The differential equation for U is then readily found by substituting Eq. (3.2) in Eq. (2.4). The result is, with the time variable conveniently rescaled as $\beta = 2Dt$:

$$\begin{aligned} -U - \beta\frac{\partial U}{\partial \beta} &= \alpha D\left(\frac{\mathbf{r}}{r^3}\right)\cdot\left[\nabla \ln P_0 - \frac{\beta}{2D}U\right] + (\mathbf{r} - \mathbf{r}_0)\cdot\nabla U \\ &\quad -\tfrac{1}{2}\beta\nabla^2 U + \tfrac{1}{4}\frac{\beta^2}{D}(\nabla U)^2, \end{aligned} \tag{3.3}$$

use having been made of the form (3.1).

The above Eq. (3.3) has been written in a form closely resembling that which can be derived from the Bloch equation for the canonical density matrix. In Appendix 1, we then follow the mathematics of this case, as set out by March and Stoddart,[5] to write down an integral equation for U (this is Eq. (A1.4)). In this integral equation, ∇U and its square appear. The approximation of prescribed diffusion assumes that U is independent of $\mathbf{r}$, so that these terms then vanish.

3.1 Approximate Solution of Integral Equation

Motivated by the above assumption, we therefore form the approximation U_1 by neglecting these quantities involving grad U inside the integrals in Eq. (A1.4). The result is then

$$\begin{aligned} \beta U_1(\mathbf{r}_0; \mathbf{r}, \beta) &= \frac{\alpha D}{2P_0(\mathbf{r}_0; \mathbf{r}, \beta)}\int d\mathbf{r}_1(\mathbf{r}_1 - \mathbf{r}_0)\cdot\frac{\mathbf{r}_1}{r_1^3}\int_0^\beta d\beta_1 P_0(\mathbf{r}, \mathbf{r}_1, \beta - \beta_1) \\ &\quad \times Q_0(\mathbf{r}_1; \mathbf{r}_0, \beta_1) \end{aligned} \tag{3.4}$$

where $Q_0 = P_0/\beta_1$. Defining the quantity J by

$$J(\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}, \beta) = \int_0^\beta d\beta_1 P_0 Q_0, \tag{3.5}$$

the evaluation of which is discussed in Appendix 1, one has finally

$$\beta U_1(\mathbf{r}_0;\mathbf{r},\beta)=\frac{\alpha D}{2P_0(\mathbf{r}_0;\mathbf{r},\beta)}\int d\mathbf{r}_1(\mathbf{r}_1-\mathbf{r}_0)\cdot\frac{\mathbf{r}_1}{\mathbf{r}_1^3}J(\mathbf{r}_0,\mathbf{r}_1,\mathbf{r},\beta). \quad (3.6)$$

Equation (A3.6) already transcends prescribed diffusion in that U_1 is plainly dependent on $\mathbf{r}$; not just on $\mathbf{r}_0$ and t as in Ref. 2. If one had reasons to seek higher accuracy, U_1 from Eq. (3.6) could now be inserted in the $\nabla_{\mathbf{r}_1}U$ terms in Eq. (A1.4) and in this way a second iterative solution U_2 could be generated.

4 SUMMARY

The main result of the present work is the approximate solution (3.4) of the Smoluchowski Eq. (2.4) for a bare Coulomb field. The claim that this solution transcends prescribed diffusion is based on the fact that this solution is dependent on $\mathbf{r}$, whereas prescribed diffusion assumes U is wholly independent of $\mathbf{r}$. Nevertheless, in writing Eq. (3.4), appeal has been made to this approximation, and further iterations may well be needed beyond Eq. (3.4) in cases when the effect of α is large.

For the future, it would seem to be of interest to make sample calculations, for fixed $\mathbf{r}_0$ and t ($\equiv\beta$) say, of the $\mathbf{r}$ dependence of U_1; as its (assumed) slow spatial variation underlies all approximations of the kinetics of the process under discussion to date. However, at the present time it would seem necessary to carry out these integrations numerically.

Should this be done in the future, it would then remain of interest to calculate the probability $W(\mathbf{r}_0, t)$ that the ion pair will remain separate at time t starting their random walk at a distance $\mathbf{r}_0$ (see Appendix 2). This is to be obtained either from Eq. (A2.6), or perhaps more directly by inserting U_1 from Eq. (3.6) into Eq. (3.2), and integrating this over $\mathbf{r}$ through the whole of space. The examples treated by Mozumder[2] should then be re-worked in order to assess the changes in the kinetics resulting from transcending prescribed diffusion. One important point is that while we expect the solution proposed here to lead back to Onsager's long-time limit $W=\exp(-\alpha/r_0)$ because, as Mozumder showed, this follows from his use of the prescribed diffusion approximation, we have not so far succeeded in obtaining this limit analytically in the method used in this paper.

Acknowledgement

The writer wishes to thank Drs N. Green and M. Pilling for some stimulating conversations on the general area in which this work lies.

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Appendix 1 Integral formulation of Smoluchowski equation

Writing the probability P in the Smoluchowski Eq. (2.4) in the product form (3.2), the function U satisfies the non-linear partial differential Eq. (3.3). The purpose of this Appendix is to transform this to an integral equation.

Using the approach of March and Stoddart,[5] one introduces the operator L given by

$$L(\mathbf{r}\mathbf{r}_0\beta) = \beta\frac{\partial}{\partial\beta} + (\mathbf{r}-\mathbf{r}_0)\cdot\nabla_{\mathbf{r}} - \tfrac{1}{2}\beta\nabla_{\mathbf{r}}^2. \tag{A1.1}$$

The equivalent integral Eq. to (3.3) may then be found using the Green function G for the operator $1 + L$:

$$G(\mathbf{r}\mathbf{r}_0\mathbf{r}_1\beta\beta_1) = \frac{P_0(\mathbf{r}\mathbf{r}_1\beta-\beta_1)P_0(\mathbf{r}_1\mathbf{r}_0\beta_1)\theta(\beta-\beta_1)}{\beta P_0(\mathbf{r}\mathbf{r}_0\beta)} \tag{A1.2}$$

where θ is the usual Heaviside function. This Green function satisfies

$$\{1 + L(\mathbf{r}\mathbf{r}_0\beta)\}G(\mathbf{r}\mathbf{r}_0\mathbf{r}_1\beta\beta_1) = \delta(\mathbf{r}-\mathbf{r}_1)\delta(\beta-\beta_1). \tag{A1.3}$$

Then one obtains the desired integral equation for U as

$$\begin{aligned} U(\mathbf{r}_0;\mathbf{r},\beta) = \int d\mathbf{r}_1\int_0^{\beta} d\beta_1\,\frac{P_0(\mathbf{r}\mathbf{r}_1\beta-\beta_1)P_0(\mathbf{r}_1\mathbf{r}_0\beta_1)}{\beta P_0(\mathbf{r}\mathbf{r}_0\beta)} \\ \times\left[\frac{\alpha D\mathbf{r}_1}{r_1^3}\cdot\left(\frac{\beta_1}{2D}\nabla_{\mathbf{r}_1}U(\mathbf{r}_1,\mathbf{r}_0,\beta_1) - \nabla_{\mathbf{r}_1}\ln P_0(\mathbf{r}_1\mathbf{r}_0\beta_1)\right.\right. \\ \left.-\frac{\beta_1^2}{4D}(\nabla_{\mathbf{r}_1}U(\mathbf{r}_1,\mathbf{r}_0,\beta_1))^2\right]. \end{aligned} \tag{A1.4}$$

To begin the iteration of this integral equation for U, one can insert the essential approximation of prescribed diffusion into the right-hand side. This corresponds to neglecting $\nabla_{\mathbf{r}_1} U$ and its square and yields a first approximation U_1 given explicitly by Eq. (3.4), when use is made of the form of P_0 in Eq. (3.1).

While Eq. (A1.4) is the main result of this Appendix, we will also discuss briefly a route to assist the evaluation of J defined in Eq. (3.5) which appears in the approximate solution (3.4) of Eq. (A1.4). Taking the Laplace transform $\mathscr{L}$ of J, one can write Eq. (3.5) as

$$\mathscr{L}J = \mathscr{L}P_0 \mathscr{L}Q_0. \qquad \text{(A1.5)}$$

Denoting the Laplace transform variable corresponding to β by E, one finds from Eq. (3.1) that

$$\mathscr{L}P_0 = \frac{\exp[-\sqrt{2E}|\mathbf{r} - \mathbf{r}_1|]}{2\pi|\mathbf{r} - \mathbf{r}_1|} \qquad \text{(A1.6)}$$

and

$$\mathscr{L}Q_0 = \frac{\sqrt{2E}}{2\pi} \frac{\exp(-\sqrt{2E}\,a)}{a^2} + \frac{1}{2\pi a^3} \exp(-\sqrt{2E}\,a) \qquad \text{(A1.7)}$$

with $a = |\mathbf{r}_1 - \mathbf{r}_0|$. Inserting Eqs (A1.6) and (A1.7) into Eq. (A1.5), one can calculate J by performing the inverse Laplace transform; the analytical closed form that has been found for J is then

$$J = \frac{1}{(2\pi\beta)^{5/2} a^2} \left[\frac{(a+b)^2}{b} + \frac{\beta}{a} \right], \qquad \text{(A1.8)}$$

with b written for $|\mathbf{r} - \mathbf{r}_1|$.

Appendix 2 Convolution form for probability that ion pair will remain separate after time *t*

Writing the product form (3.2) as

$$P = P_0 F \qquad \text{(A2.1)}$$

let us define its Fourier transform on $\mathbf{r}$ by

$$W(\mathbf{r}_0; \mathbf{p}, t) = \int P(\mathbf{r}_0; \mathbf{r}, t) \exp(-i\mathbf{p} \cdot \mathbf{r}) d\mathbf{r}. \qquad \text{(A2.2)}$$

The Fourier transform of a product has the form of a convolution and hence, writing

$$\tilde{P}_0(\mathbf{r}_0; \mathbf{p}, t) = \int P_0(\mathbf{r}_0; \mathbf{r}, t) \exp(-i\mathbf{p} \cdot \mathbf{r}) d\mathbf{r} \tag{A2.3}$$

with a corresponding definition for $\tilde{F}$, one can express Eq. (A2.2) in the alternative form

$$W(\mathbf{r}_0; \mathbf{p}, t) = \int \tilde{P}_0(\mathbf{r}_0, \mathbf{p}' - \mathbf{p}, t)\tilde{F}(\mathbf{r}_0, \mathbf{p}', t) d\mathbf{p}'. \tag{A2.4}$$

The desired probability that the ion pair will remain separate at time t, starting their random walk at a distance $\mathbf{r}_0$ is

$$W(\mathbf{r}_0, 0, t) = \int P(\mathbf{r}_0; \mathbf{r}, t) d\mathbf{r} \tag{A2.5}$$

which, from Eq. (A2.4) is given by

$$W(\mathbf{r}_0, 0, t) = \int \tilde{P}_0(\mathbf{r}_0; \mathbf{p}', t)\tilde{F}(\mathbf{r}_0; \mathbf{p}', t) d\mathbf{p}'. \tag{A2.6}$$

As t tends to zero, $\tilde{P}_0$ tends to unity, and hence

$$W(\mathbf{r}_0; 0, 0) = 1 = \int \tilde{F}(\mathbf{r}_0; \mathbf{p}', t) d\mathbf{p}'. \tag{A2.7}$$

In contrast, in the long time limit, F becomes independent of $\mathbf{r}$, and one must regain Onsager's result[1]

$$\lim_{t \to \infty} W(\mathbf{r}_0, 0, t) = \exp(-\alpha/r_0) \tag{A2.8}$$

as the steady-state solution.